Chemistry of Triple-Decker Sandwich Complexes Containing Four-Membered Open B2E2 Rings (E = S or Se)


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Chemistry of Triple-Decker Sandwich Complexes Containing Four-Membered Open B$_2$E$_2$ Ring (E = S or Se)


Abstract: Building upon our earlier studies on cobaltaheteroboranes, we explored the chemistry with heavier group 9 metals. Reaction of [Cp*M(M-Cl)]$_2$ (Cp*=η$^5$-C$_5$Me$_5$; M = Co, x = 0; M = Rh or Ir, x = 1) with [LiBH$_4$·THF] followed by thermolysis with excess of chalcogen powders (S or Se) afforded dimetallaheteroboranes nido-[Cp*M$_2$B$_2$E$_2$], 1-4 (1: E = S, 2: E = Se, M = Co; 3-4: E = Se, M = Rh and Ir) in moderate to good yields. The solid state X-ray structures of these compounds show open-cage triple decker clusters.

The development towards the large number of metallaheteroborane have gained pronounced deal of interest owing to their utility in the preparation of high-nuclearity clusters.[6] Among them, group 9 metallaheteroboranes have received significant attention due to their applications in catalysis.[7-8] For example, nido-rhodathiaborane [8,8,8-(PPH$_3$)$_2$H-9-(NC$_5$H$_5$)-nido-8,7-RhSB$_2$H$_3$] acts as a catalyst for the isomerization and hydrogenation of alkenes.[8c] Although, metallaheteroboranes comprised of thia[9,10] and azal[11] ligands have been explored, compounds that contain heavier heteroatoms such as selenolato[12] and telluro[13] ligands are relatively limited. As a result, we[5a-c,11] and others[9,10] have synthesized interesting metallaheteroborane clusters containing selenium and tellurium that illustrate different reactivity and structural patterns as compared to sulfide clusters.[12]

In the past several years, we have been actively involved in the synthesis of metallaheteroboranes containing heavier chalcogen atoms that enabled us to synthesize a series of group 5[11,13] and 6[8c,11,14,15] metallaheteroboranes through the activation of diorganyldichalcogenide ligands or chalcogen powders. For example, group 6 dimetallaheteroboranes [(Cp*Co)$_2$B$_2$H$_4$][CuCl$_2$]$_2$[13c,12a] (E = Te, m = 0, n = 1; E = S or Se, m = 1, n = 0) show diverse reactivity patterns towards many metal carbonyls yielding metallaheteroboranes containing six-membered middle ring.[14c,16] Grimes reported the first neutral and air stable cobalt triple decker compounds [(Co$_2$CO)$_2$B$_2$H$_3$] (R = Me/H), inclosing a central [RC$_2$B$_3$H$_4$]$_n$ ring.[18] Recently, we have also reported various triple-decker compounds [(Cp*Mo)$_2$][µ-η$^4$-B$_2$H$_4$ERu(CO)$_3$]$_2$ from the reaction of [(Cp*Mo)$_2$B$_2$H$_4$E] (E = S and Se) and [Ru(OC$_3$)$_3$]$_2$.[19] Synthesis of [(Cp*Co)$_2$B$_2$H$_3$] by Sneddon[18] and our recent studies on [(Cp*Co)$_2$B$_2$H$_4$] (1: E = S; 2: E = Se)[19,20] led us to explore the chemistry of heavier group 9 metals. Thus, analogous the rhodium and iridium systems became of interest. In this report, we describe the synthesis and chemistry of group 9 triple decker sandwich metallaheteroboranes containing four-membered open B$_2$E$_2$ central ring (E = S or Se).

Results and Discussion

Syntheses of group 9 open triple decker compounds

As shown in Scheme 1, the reaction of [Cp*M(M-Cl)]$_2$ (M = Rh or Ir) and [LiBH$_4$·THF] followed by thermolysis in presence of Se powder yielded corresponding dimetallaheteroboranes nido-[Cp*M$_2$B$_2$H$_3$Se], 3 (M = Rh, 4: M = Ir) in moderate yields.[21] The identity of these dimetallaheteroboranes was unambiguously established by multinuclear NMR spectroscopy, HR-MS, FT-IR, X-ray crystallography and computational analysis (DFT). The $^{13}$C($^1$H) NMR spectrum of 3 reveals a sharp signal at δ = 23.9 ppm which is downfield shifted as compared to 4 (δ = 7.3 ppm) but upfield shifted as compared to 1 (δ = 33.5 ppm). The $^{1}$H($^{13}$B) spectra of 3 and 4 display resonances at δ = 4.50 and 2.98 ppm respectively for B-H. Further, the $^{1}$H($^{13}$B) and $^{13}$C($^1$H) NMR support the presence Cp* ligand.

Introduction

The chemistry of metallaheteroboranes traditionally achieved by the reaction of polyhedral heteroborane anions with metal fragments or the incorporation of heteroatom into metallahaborane clusters.[11-9] The developments towards the large numbers of metallaheteroborane have gained pronounced deal of interest owing to their utility in the preparation of high-nuclearity clusters.[6] Among them, group 9 metallaheteroboranes have received significant attention due to their applications in catalysis.[7-8] For example, nido-rhodathiaborane [8,8,8-(PPH$_3$)$_2$H-9-(NC$_5$H$_5$)-nido-8,7-RhSB$_2$H$_3$] acts as a catalyst for the isomerization and hydrogenation of alkenes.[8c] Although, metallaheteroboranes comprised of thia[9,10] and azal[11] ligands have been explored, compounds that contain heavier heteroatoms such as selenolato[12] and telluro[13] ligands are relatively limited. As a result, we[5a-c,11] and others[9,10] have synthesized interesting metallaheteroborane clusters containing selenium and tellurium that illustrate different reactivity and structural patterns as compared to sulfide clusters.[12]

In the past several years, we have been actively involved in the synthesis of metallaheteroboranes containing heavier chalcogen atoms that enabled us to synthesize a series of group 5[11,13] and 6[8c,11,14,15] metallaheteroboranes through the activation of diorganyldichalcogenide ligands or chalcogen powders. For example, group 6 dimetallaheteroboranes [(Cp*Co)$_2$B$_2$H$_4$][CuCl$_2$]$_2$[13c,12a] (E = Te, m = 0, n = 1; E = S or Se, m = 1, n = 0) show diverse reactivity patterns towards many metal carbonyls yielding metallaheteroboranes containing six-membered middle ring.[14c,16] Grimes reported the first neutral and air stable cobalt triple decker compounds [(Co$_2$CO)$_2$B$_2$H$_3$] (R = Me/H), inclosing a central [RC$_2$B$_3$H$_4$]$_n$ ring.[18] Recently, we have also reported various triple-decker compounds [(Cp*Mo)$_2$][µ-η$^4$-B$_2$H$_4$ERu(CO)$_3$]$_2$ from the reaction of [(Cp*Mo)$_2$B$_2$H$_4$E] (E = S and Se) and [Ru(OC$_3$)$_3$]$_2$.[19] Synthesis of [(Cp*Co)$_2$B$_2$H$_3$] by Sneddon[18] and our recent studies on [(Cp*Co)$_2$B$_2$H$_4$] (1: E = S; 2: E = Se)[19,20] led us to explore the chemistry of heavier group 9 metals. Thus, analogous the rhodium and iridium systems became of interest. In this report, we describe the synthesis and chemistry of group 9 triple decker sandwich metallaheteroboranes containing four-membered open B$_2$E$_2$ central ring (E = S or Se).

Results and Discussion

Syntheses of group 9 open triple decker compounds

As shown in Scheme 1, the reaction of [Cp*M(M-Cl)]$_2$ (M = Rh or Ir) and [LiBH$_4$·THF] followed by thermolysis in presence of Se powder yielded corresponding dimetallaheteroboranes nido-[Cp*M$_2$B$_2$H$_3$Se], 3 (M = Rh, 4: M = Ir) in moderate yields.[21] The identity of these dimetallaheteroboranes was unambiguously established by multinuclear NMR spectroscopy, HR-MS, FT-IR, X-ray crystallography and computational analysis (DFT). The $^{13}$C($^1$H) NMR spectrum of 3 reveals a sharp signal at δ = 23.9 ppm which is downfield shifted as compared to 4 (δ = 7.3 ppm) but upfield shifted as compared to 1 (δ = 33.5 ppm). The $^{1}$H($^{13}$B) spectra of 3 and 4 display resonances at δ = 4.50 and 2.98 ppm respectively for B-H. Further, the $^{1}$H($^{13}$B) and $^{13}$C($^1$H) NMR support the presence Cp* ligand. The mass
spectra of 3 and 4 show molecular ion peaks (ESI+ at m/z 682.8986 and 841.0363 respectively. These spectroscopic data validate the existence of C2 symmetry in these molecules.

Single crystals of 3 and 4 suitable for analysis were obtained from the hexane/CH2Cl2 solution at 3 °C. By changing the metal to heavier metal Ir, compound 4 crystallized in C2/c space group rather than P21/c. The solid state structures of 3 and 4 represents an open-cage triple decker in which two metals are sandwiched between the open [B2Se2] ring and two Cp* ligands (Figure 1). The vertical mirror plane along the C2 axis, bisects the B1-B2 bond which provides a C2v symmetry in the molecule. Alternatively, this geometry can be described as pentagonal bipyramid, in which one of the atoms is missing at the equatorial plane. According to the Wade-Mingos electron counting rule, [22] this nido-open-cage geometry consistent with 8 sep, [2(Cp*M) X 2 + 2(BH) X 2 /2] (M = Rh or Ir). As shown in Figure 1, overall the structures of 3 and 4 are similar to that of [(Cp*Co)2B3H7]2+ [20]. The two Ir atoms in 4 are separated by 3.465 Å, which is comparatively longer as compared to Rh-Rh (3.416 Å) and Co-Co (3.144 Å) distances. Similarly the B-Se distance of 1.998(8) Å in 4 is relatively longer as compared to 3 (1.983(3) Å) and 2 (1.985(6) Å). Although the B1-B2 distances of 1.746(10) Å for 4 and 1.739(4) Å for 3 fall within the standard range, [20,23] the M-B (M = Rh or Ir) bond lengths are comparatively shorter as compared to those of related metallaborane clusters. [23b-d]

Density functional theory (DFT) calculations were used to probe the reactivity patterns of 2-4 at the PBE0/Def2-TZVP level of theory. The bond lengths and the NMR chemical shift values of 2-4 closely matched with those of the experimental values (Tables S1 and S2). The molecular orbital study of 2-4 shows that the HOMO-LUMO energy gap increases in the order of 2 < 3 < 4 (Figure 2, Table S3), which is consistent with their thermodynamic stability. In addition, a significant destabilization of HOMO of 2, suggests a higher reactivity compared to 3 and 4. Inspection of electron density of the FMOs of 2-4 reveals that HOMOs are predominantly localized on metal and Se atoms. Further, the shapes of HOMO-3 and LUMO+3 of 2-4 disclose the bonding and anti-bonding interactions between the boron and metal centers (Figure S30). The B-B and M-Se Wiberg bond indices for 2-4 were found to be close to 0.7 and 1.04 respectively in all cases. However, the M-M Wiberg bond indices for 2-4 were close to 0.07 that indicate absence of bonding interaction between two metal centers (Table S4).

Examples of metallaheteroborane clusters with heavier group 16 elements, especially Te atom are limited. [14d,16] Thus, to isolate tellurium analogue of nido-1, we have performed the reaction of [Cp*CoCl]2 and [LiBH4·THF] followed by thermolysis with Te powder. In contrast to the earlier results, this reaction led to the formation of a nido-[(Cp*Co)2B3H5Te2], 5 and [(Cp*Co)2B3H5]2+ (Scheme 2). All of our attempts to isolate the Rh and Ir analogues of 5 were failed. The reaction yielded all known clusters, such as [(Cp*Rh)2B3H5]2+ and [Cp*IrH4]2+ in low
yields respectively. Compound 5 was isolated as violet crystals and characterized by the NMR spectroscopy, mass spectrometry, X-ray diffraction and DFT studies.

![Scheme 2. Synthesis of cluster 5.](image)

Compound 5 crystallizes in monoclinic C2/c space group in which the asymmetric unit consists of two Co atoms each ligated to Cp* ligand, two B-H units and two µ-Te atoms. The molecular structure of 5, shown in Figure 3, shows that the cage geometry is mono-capped square antiprism comparable to that of \([\text{Ni}_5\text{C}(\text{CO})_7]^{2-}\) \([22]\) having an interstitial carbon atom at the center. According to the cluster electron-counting rules,\([22]\) compound 5 possesses 11 skeletal electron pairs (sep) \([2(\text{Cp}^*\text{Co}) \times 2 + 4(\mu-\text{Te}) \times 2 + 2(\text{BH}) \times 5)/2\) and thus it obeys Wade rules. Cluster 5 has \(C_{2v}\) symmetry with two Co and two Te atoms in the open cage. Among the five boron atoms, one of the boron atoms is capped by four other boron atoms, which is in a plane of the mono-capped square antiprism. The molecule has no direct Co-Co (\(d_{\text{Co-Co}} = 3.645\) Å) and Te-Te (\(d_{\text{Te-Te}} = 3.406\) Å) bonds (Figure 3).

Although the B-B and Co-B bond distances fall in the range observed for other characterized cobaltaboranes,\([19,20,24]\) the Co-Te bond distance of 2.5019(6) Å is significantly longer as compared to other telluraboranes, e.g., \([[\text{CpMo}_2\text{B}_4\text{H}_4\text{Te}_2]](d_{\text{B-Te}} = 2.033(11)^{[14a]}\text{ and } 2.299(13)\) Å) and \([[\text{Cp}^*\text{Mo}]_2(\mu-\eta^5:\eta^5-\text{B}_3\text{H}_2\text{TeCo}(\text{CO}))]\) \(d_{\text{Mo-Mo}} = 2.238(7)\) Å\([14c]\).

![Figure 3. Molecular structure of 5. Selected bond lengths (Å) and angles (º): Co1-Te1 2.5019(6), Te1-B1 2.347(5), Te1-B2 2.347(5), Co1-B1 2.154(5), Co1-B2 2.149(5), B1-B2 1.824(8), B2-B1 2.015(6), B1-B3 1.680(6), B3-B2 1.680(6), B(1)-Co1(1)-Te(1) 94.42(14), B(1)-Te(1)-B(2) 50.85(16), B(1)-B(3)-B(2) 73.7(3).](image)

Consistent with the solid state X-ray structure determination, the room temperature \(^1\text{H}\) NMR spectrum reveals two types of boron chemical shifts at \(\delta = -3.6\) and -8.5 ppm in 4:1 ratio. The \(^1\text{H}\) NMR spectrum shows two singlet peaks that correspond to two types of B-H terminal protons appeared at \(\delta = 6.00\) and 2.96 ppm. The combination of \(^1\text{H}\) NMR and \(^13\text{C}\{1\text{H}\}\) NMR spectra also reflects the presence of symmetry in the molecule.

To gain insight into the electronic structure and bonding of 5, we have carried out geometry optimization of 5 (Cp analogue of 5) by DFT methods (Figures 4a-b). The calculated Co1-Co1 and Te1-Te1 distances of 3.638 and 3.442 Å respectively are in good agreement with the experimental data obtained from the solid state X-ray structure \(d_{\text{Co-Co}} = 3.645\) and \(d_{\text{Te-Te}} = 3.406\) Å. Accordingly, the computed distance of 2.321 Å for B1-Te1 bond is very close to the experimental data of 2.347(5) Å. The topological analysis of the electron density of Co1-Te1-Co1-Te1 plane indicates the occurrence of BCPs along the Co-Te bond paths (Figure 4c). As expected, no BCPs were observed for Co1-Co1 and Te1-Te1 atom pairs indicating 5 with no direct bonds between two Co atoms and two Te atoms. Thus, compound 5 unveils a nido cluster that can be accessed from a 10 vertex bicapped square antiprism by removing one of the capped vertices.

![Figure 4. (a) and (b) Illustration of optimized geometry of 5 in different orientations, (c) Contour line diagrams of the Laplacian of the electron density, \(\nabla^2\rho(r)\) of Co1-Co1-Te1-Te1 in 5 that generated using the Multiwfn program package at the PBE0/Def2-TZVP level of theory.](image)

**Reactivity of nido-1 and nido-2 with [Ru_3(CO)_12]**

Earlier, Fehlner and co-workers have demonstrated that the central open ring of \([[\text{Cp}^*\text{Re}_2\text{B}_4\text{H}_8]]^{[29]}\) can be closed if this is treated with \([\text{BHCl}_2\cdot\text{SMMe}_2]\) or \([\text{Co}_2(\text{CO})_8]\). The reactions led to the formation of triple-decker complexes \([[\text{Cp}^*\text{Re}_2(\mu-\eta^5:\eta^5-\text{B}_3\text{H}_2\text{Cl})]]^{[29]}\) and \([[\text{Cp}^*\text{Re}_2(\mu-\eta^5:\eta^5-\text{B}_3\text{H}_2\text{Co}(\text{CO}))]]^{[31]}\) respectively that contain six-membered ring as the middle-deck. In a similar fashion, Barton has synthesized closo-[\(\text{B}_6\text{H}_4\text{Cl}_2]\) \([30]\) and \([[\text{Cp}^*\text{Re}_2(\mu-\eta^5:\eta^5-\text{B}_3\text{H}_2\text{Cl})]\)]\([32]\) Therefore, we planned to close the central open ring of nido-1 and nido-2 by reacting them with \([\text{Ru}_3(\text{CO})_{12}]\). The reactions indeed led to the formation of closo-\([[\text{Cp}^*\text{Co}]_2(\mu-\eta^5:\eta^5-\text{B}_3\text{H}_2\text{E}_2-\text{Ru}(\text{CO})_2]_{\text{Ru}(\text{CO})_2(\mu-\text{Ru}(\text{CO})_2)}\),
The molecular structure of 7, shown in Figure 5a, is consistent with the spectroscopic data. The core geometry of 7 is that of a pentagonal bipyramid in which one exopolyhedral Ru(CO)₄ moiety is bonded with two Ru atoms of 7 (Figure 5a). The molecule possesses a planar five-membered (B₂Se₂Ru) ring, which is sandwiched between Cp*Co and [Ru(CO)₂(B₂H₂Se₂)] moieties (the mean plane deviation is 0.18 Å and sum of internal terminal B-H protons. The presence of Cp* ligand has also been shown molecular ion peaks (ESI+) at m/z = 812.7104 and 930.5797 respectively. The IR spectra show strong absorption bands at 1997, 1934 cm⁻¹ for 6 and 2002, 1924 cm⁻¹ for 7 that correspond to terminal carbonyl groups.

Reactivity of nido-2 and nido-3 with \(\text{[Fe}_2\text{(CO)}_3]\)

Metallocenes and cyclophanes are some of the most systematically studied sandwich molecules in organometallic and organic chemistry.\(^{36,37}\) The precedence of structurally characterized sandwich molecules in metallaborane and metallahetroborane chemistry are rare. Thus, in order to afford the iron analogue of 6 and 7, we carried out the reactions of nido-2 and nido-3 with \(\text{[Fe}_2\text{(CO)}_3]\), as shown in Scheme 4, room temperature reactions of them with \(\text{[Fe}_2\text{(CO)}_9]\) resulted in the formation of nido-[\(\text{[Cp}^*\text{M}(\text{CO})_3\text{B}_3\text{H}_6\text{Se}_2]\), 8-9 (M = Co; 9: M = Rh) and \(\text{[Cp}^*\text{Co} \text{Fe}_2\text{(CO)}_3\text{Se}_2]\). 10 and \(\text{[Cp}^*\text{Co} \text{Fe}_2\text{(CO)}_3\text{Se}]\), 11. Interestingly, compound 9 is considered to be an analogue of 8.\(^{20}\)

Compound 9 is fully characterized by mass spectrometry and multinuclear NMR spectroscopy. The \(^{11}\text{B}(^1\text{H})\) NMR spectrum of
Figure 6. (a): Contour line diagrams of the Laplacian of the electron density, $\nabla^2 \rho(r)$ of central ring Ru2-Se1-B1-B2-Se2 in 7 that generated using the Multiwfn program package at the PBE0/Def2-TZVP level of theory; (b-f): Illustration of molecular orbitals showing various bonding interactions. Solid red lines indicate areas of charge concentration ($\nabla^2 \rho(r) > 0$), while dashed gray lines show areas of charge depletion ($\nabla^2 \rho(r) < 0$). Solid brown lines indicate bond paths and blue dots indicate BCPs.

9 shows a sharp singlet at $\delta = 22.2$ ppm, which is upfield shifted relative to 8 ($\delta = 31.2$ ppm). The $^1$H($^1$B) NMR spectrum show one type of Cp* protons at $\delta = 1.78$ ppm along with B-H at $\delta = 5.69$ ppm. The mass spectrometric data ($m/z$ 562.8160) suggest a molecular formula of [(Cp*Rh)Fe(CO)$_3$B$_2$H$_2$Se$_2$]. The FT-IR spectrum displayed stretching frequency for CO ligands at 2054, 1997 cm$^{-1}$ and for B-H at 2571 cm$^{-1}$. Both the experimental and the theoretical data (Tables S1 and S2) confirm the existence of plane of symmetry in 9.

The X-ray quality crystals of 9 were obtained from hexane-layered CH$_2$Cl$_2$ solution at 3 °C. The solid-state X-ray structure of 9, shown in Figure 7, features pentagonal bipyramidal geometry with a missing equatorial vertex. Although the Fe-B bond distance is shorter (2.199(6) Å) as compared to 8, the B-B and B-Se bond lengths fall within the range.[19,20]

Scheme 4. Reactivity of dimetallaseelenaboranes with group 8 metal carbonyl compounds.

In parallel to the formation of 8, reaction of nido-2 with [Fe$_2$(CO)$_9$]$_3$ yielded compounds 10 and 11, isolated as air stable green and brown solids in low yields (Scheme S1, Supporting information). Note that reaction of nido-3 with [Fe$_2$(CO)$_9$]$_3$ led to the formation of 9. Compounds 10 and 11 were characterized by the $^1$H, $^{13}$C($^1$H) NMR spectroscopy, mass spectrometry and X-ray crystallography. The $^1$H NMR spectra of 10 and 11 display one type of Cp* protons. Further, presence of Cp* ligands have also been supported by $^{13}$C($^1$H) NMR spectra.

The solid state X-ray structure of 10, shown in Figure S1, confirms the structural inferences made on the basis of the spectroscopic results. The molecular structure of 10 represents a new heterometallic chalcogenide cluster where the prime cluster constituents are Co, Fe and Se atoms. The asymmetric unit of 10 consist of one Co atom bonded to a Cp* ligand and three {Fe(CO)$_2$} moieties which are connected through two $\mu_4$-bridging CO ligands. The Co1-Fe2-Fe1 ring bonded with two $\mu_7$-Se atoms (Figure S1, supporting information). Overall, the core geometry of 10 can be visualized as an octahedral geometry with two bridging CO units. Compound 11 crystallizes in the monoclinic C2/c space group with the asymmetric unit consisting of one Co atom bonded to a Cp* ligand (Figure S2). The core geometry of 11 can also be well visualized as a trigonal bipyramid where the equatorial plane consists of [CoFe$_2$] trimetallic unit.

Reactivity of nido-8 with [Ru$_3$(CO)$_{12}$]

In order to close the central open ring of nido-8, we treated it with [Ru$_3$(CO)$_{12}$] that indeed closed the central open ring to yield brown crystalline solid, closo-[{(Cp*Co)$_3$$\mu_7$-$\eta^2$:B$_2$H$_2$Se$_2$Ru(CO)$_2$}]
Ru(CO)₅[μ-Fe(CO)₅]), 12 in 19% yield (Scheme 4). The ¹¹B{¹H} NMR spectrum of 12 displays one resonance at δ = 23.0 ppm, similar to 6 and 7. The IR spectrum of 12 features strong absorptions at 2054 and 1997 cm⁻¹ corresponds to the terminal carbonyl groups. The mass spectrum of 12 shows molecular ion peaks (ESI⁺) at m/z = 862.6298. In order to confirm the spectroscopic assignments and to determine the solid state structure of 12, the X-ray diffraction analysis was undertaken. The crystal structure corresponds to a pentagonal bipyramidal core consisting of Ru and Fe atoms. The molecular structure, shown in Figure 5b, is fully consistent with the solution spectroscopic data. The core geometry of 12 is similar to that of 7 with a different exo fragment e.g., Fe(CO)₅ moiety. The molecule possesses a planar [μ-η⁴:η⁴-Si₂B₂H₆Se₂Ru(CO)₅] ring (mean plane deviation 0.20 Å), sandwiched between Ru₃CO unit and [Ru(CO)₅(μ-Fe(CO)₅)] fragment.

Conclusions

In conclusion, we have described the synthesis and chemistry of metallaheteroboranes ([Cp*M]₂B₄H₆E₅] (M = Rh and Ir; E = Se), which are analogous of [[Cp*Co]₂B₄H₆E₅] (E = S, Se). Further, we have shown the utility of these molecules to generate triple-decker sandwich metallaheteroboranes upon reaction with [Ru₂(CO)₅]. In addition, we have isolated and structurally characterized a novel 9-vertex nido-[Cp*Co]₂B₂H₅Te₂ that represents a new metallaheteroborane containing heavier chalcogen (Te) atom.

Experimental Section

General Procedures and Instrumentation: All the operations were conducted using standard Schlenk techniques under an Ar/N₂ atmosphere. Solvents were predistilled under Argon. All other reagents Cp*H, CoCl₂, n-BuLi in hexane, [LiBH₄·THF], S, Se, Te powders, [Fe₂(CO)₉] and [Ru₃(CO)₁₂] (Aldrich) were used as received. [Cp*Co(µ-Cl)]₂, [Cp*Rh(µ-Cl)₂], [Cp*Ir(µ-Cl)₂], nido-1, nido-2, nido-8, nido-9, and the external reference, [Bu₄N][B₃H₈], for the ¹¹B NMR were synthesized by the literature methods. Thin layer chromatography was carried on 250 mm diameter aluminium supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded on 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ, ppm, CDCl₃, 7.26), while a sealed tube containing [Bu₄N(B₃H₈)] in C₆D₆ (δ, ppm, 25.2), was used as an external reference for the ¹¹B NMR. Mass spectra were recorded in a Bruker Micro TOF-II mass spectrometer in ESI ionization mode.

Synthesis of 3: In a flame-dried Schlenk tube, the brown solution of [Cp*Rh(µ-Cl)₂] (0.100 g, 0.12 mmol) in toluene (12 mL), [LiBH₄·THF] (0.6 mL, 1.25 mmol) and S powder (0.020 g, 0.62 mmol) yielded yellow [Cp*IrH₄] as major product.[20]

4. HRMS (ESI⁺): m/z calculated for C₂₀H₃₂B₂Rh₂Se₂Na [M + Na⁺] found: 682.9898; ¹¹B{¹H} NMR (160 MHz, CDCl₃, 22 °C): δ = 23.9 (s, 2B); ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 99.6 (s, C₅Me₅), 10.0 (s, C₅Me₅); IR (CDCl₃, cm⁻¹): 3 = 2560 (BH⁻).

Synthesis of 4: In a flame-dried Schlenk tube, the yellow solution of [Cp*Ir(µ-Cl)₂] (0.100 g, 0.12 mmol) in toluene (12 mL), [LiBH₄·THF] (0.6 mL, 1.25 mmol) and S powder (0.020 g, 0.62 mmol) yielded yellow complex [Cp*IrH₄] as major product.[20]

5. HRMS (ESI⁺): m/z calculated for C₂₀H₃₂B₂Rh₂Se₂Na 730.9928 [M + Na⁺] found: 730.9910; ¹¹B{¹H} NMR (160 MHz, CDCl₃, 22 °C): δ = 3.6 (s, 4B); ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 179 (s, 30H, C₅Me₅), 29.7 (s, 4B-H), 6.00 ppm (s, 1B-H); ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 92.5 (s, C₅Me₅), 10.9 ppm (s, C₅Me₅); IR (CDCl₃, cm⁻¹): 3 = 2497 (BH⁻).

Synthesis of 6 and 7: In a flame-dried Schlenk tube, nido-[Cp*Co]₂B₂H₅Se₂, 2 (0.160 g, 0.12 mmol) was dissolved in toluene (6
In a similar reaction conditions, the reaction of nido-2 (0.060 g, 0.105 mmol) with [Ru2(CO)3] (0.067 g, 0.105 mmol) led to the isolation of the green, 7 (0.031 g, 32%). Similar reaction work up and purification methods were employed for compound 7 as employed for the compound 6.

6. HRMS (ESI+): m/z calculated for C41H38B2CoRu2O5SeNa 812.7092 [M + H]+, found: 812.7104; 13C{1H} NMR (125 MHz, CDCl3, 22 °C): δ = 19.9 (s, 2B); 13C{1H} NMR (125 MHz, CDCl3, 22 °C); δ = 1.66 (s, 15H, Cp*), 4.98 (s, 2B-H); 13C{1H} NMR (125 MHz, CDCl3, 22 °C); δ = 197.1 (s, C5Me5), 12.2 (s, C5Me5); IR (DCM, cm\(^{-1}\)): v = 2523 (BH), 1997, 1934 (terminal C=O stretching).

7. HRMS (ESI+): m/z calculated for C41H38B2CoRu2O5SeNa 930.5800 [M + Na]+, found 930.5797; 13C{1H} NMR (125 MHz, CDCl3, 22 °C): δ = 22.3 (s, 2B); 13C{1H} NMR (500 MHz, CDCl3, 22 °C); δ = 1.66 (s, 15H, Cp*), 6.05 (s, 2B-H); 13C{1H} NMR (125 MHz, CDCl3, 22 °C): δ = 197.1 (CO), 93.7 (s, C5Me5), 11.3 (s, C5Me5); IR (DCM, cm\(^{-1}\)): v = 2539 (BH), 2080, 2002, 1924 (terminal CO stretching).

Synthesis of 9. In a flame-dried Schlenk tube, nido-[(Cp*Rh)B2H2Se2], 3 (0.080 g, 0.091 mmol) and [Fe2(CO)9] (0.203 g, 0.448 mmol) were dissolved in hexane (10 mL) and allowed to stir at room temperature for 3 hours. After the removal of the solvent the resultant residue was chromatographed on silica gel TLC plates. Elution with a hexane–CH2Cl2 (70:30, v/v) mixture yielded air stable brown [Cp*Rh]Fe(Ru)B2H2Se2, 12 (0.019g, 19%) and green [Cp*Ru(CO)5B2H2Se2], 7 (0.016 g, 14%).

X-ray crystal structure determinations. Crystal diffraction data of 3 and 7 were collected and integrated using a D8 VENTURE Bruker AXS diffractometer, with multilayer monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods using the SIR92[1] program and then refined with full-matrix least-squares methods based on F2[SHELXL-2014][2] with the aid of the WINGX program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters, except boron-linked hydrogen atoms that were introduced in the structural model through Fourier difference map analysis. Hydrogen atoms were finally included in their calculated positions.

Crystal data for 3: CCDC 1586318, C20H32B2Rh2Se2, M = 657.81, monoclinic, P21/c, a = 11.0070(13) Å, b = 16.043(2) Å, c = 14.1958(18) Å, β = 112.055(4)°, V = 2523.3(5) Å3, Z = 4, μ = 1.881 mg/m3, μ = 4.556 mm\(^{-1}\). F(000) = 1280, R1 = 0.0216, wR2 = 0.0493, 5302 independent reflections [29 ≤ 50.48°] and 251 parameters, Goodness-of-fit on F2 = 1.087.

Crystal data for 4: CCDC 1586319, C20H32B2Ir2Se2, M = 836.39, monoclinic, C2/c, a = 20.8525(5) Å, b = 15.1280(4) Å, c = 16.3205(3) Å, β = 108.2660(11)°, V = 4902.9(2) Å3, Z = 4, μ = 3.213 mg/m3, μ = 14.105 mm\(^{-1}\). F(000) = 702.59, R1 = 0.0261, wR2 = 0.0526, 4234 independent reflections [28 ≤ 49.994°] and 245 parameters, Goodness-of-fit on F2 = 0.987.

Crystal data for 5: CCDC 1560400, C20H32B2Co2Te2, M = 702.59, monoclinic, C2/c, a = 15.4187(12) Å, b = 8.1411(5) Å, c = 20.9382(2) Å, β = 107.167(4)°, V = 2511.2(3) Å3, Z = 4, μ = 1.585 mg/m3, μ = 3.604 mm\(^{-1}\). F(000) = 1352, R1 = 0.0249, wR2 = 0.0585, 2216 independent reflections [29 ≤ 49.99°] and 132 parameters, Goodness-of-fit on F2 = 1.060.

Crystal data for 7: CCDC 1560396, C21H17B2Co2Ru2Se2, M = 902.99, orthorhombic, P2222, a = 10.892510(5) Å, b = 14.02413(1) Å, c = 16.8708(1) Å, V = 2578.2(4) Å3, Z = 4, μ = 2.326 mg/m3, μ = 5.219 mm\(^{-1}\). F(000) = 1704, R1 = 0.0195, wR2 = 0.0420, 5834 independent reflections [29 ≤ 54.96°] and 319 parameters, Goodness-of-fit on F2 = 1.079.
Crystal data for 9: CCDC 1560399, C$_{18}$H$_{17}$B$_{2}$CoFeO$_{8}$Ru$_{2}$Se$_{2}$, $M_r$ = 857.77, monoclinic, $P2_1/n$, $a$ = 8.7864(2) $\AA$, $b$ = 17.5214(4) $\AA$, $c$ = 17.3426(4) $\AA$, $\beta$ = 99.5134(10)$^\circ$, $V$ = 2633.171(10) $\AA^3$, $Z$ = 4, $\rho_{\text{calc}}$ = 2.164 mg/m$^3$, $\mu$ = 5.088 mm$^{-1}$, $F(000)$ = 1632, $R_I$ = 0.0309, $wR_2$ = 0.0654, 4639 independent reflections [28 ≤ 50.00$^\circ$] and 320 parameters, Goodness-of-fit on $F^2$ = 1.018.

Computational Details. Quantum chemical calculations using DFT methods were carried out on compounds 2-4, 5' and 7-9 (Cp analogue) as employed in the Gaussian09 package.

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Note that, similar reactions have been carried out in presence of S powder, which led to the formation of known compounds as well as other unknown compounds with poor yields, which we couldn’t isolate.


X. Lei, A. K. Bandyopadhyay, M. Shang, T. P. Feulner, Organometallics 1999, 18, 2294-2296.


The topological parameters calculated for the Ru2-Se1, Ru2-Se2, B1-B2, B1-Se1 and B2-Se2 bond paths in Ru2-Se1-B1-B2-Se2 plane i.e., the electron density ρ at the bond critical points (BCPs (3-1)), the Laplacian of the density $\nabla^2 \rho$ are listed in Table S5.
Synthesis of group 9 triple decker sandwich metallaheteroboranes containing four-membered open B₂E₂ central ring (E = S or Se) has been described. Further, the reactivity of these molecules with group 8 metal carbonyl compounds has been carried out that yielded closo-polyhedral metallaheteroboranes.


Chemistry of Triple-Decker Sandwich Complexes Containing Four-Membered Open B₂E₂ Ring (E = S or Se)